Half-Heusler compounds: materials for thermoelectric applications

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Optimizing the carrier concentration or reducing the thermal conductivity are the main keys to enhance the thermoelectric properties of materials. We optimized the carrier concentration of the *p*-type half-Heusler alloy $Ti_{0.3}Zr_{0.35}Hf_{0.35}CoSb_{1-x}Sn_x$ by partial substitution of Sb by Sn. A maximal figure of merit of zT = 0.8 was achieved for a substitution level of 15% Sn. Thermoelectric performance of the *p*-type half-Heusler series $Ti_{1-x}Hf_xCoSb_{0.85}Sn_{0.15}$ was improved by tuning the intrinsic microstructure of the phase separation, which is one way to decrease the lattice thermal conductivity. A record thermoelectric figure of merit of zT = 1.2 was achieved for the composition $Ti_{0.25}Hf_{0.75}CoSb_{0.85}Sn_{0.15}$. To investigate the long-term stability of the phase separation in half-Heusler alloys, the thermal cycling of the compound with a composition of $Ti_{0.5}Hf_{0.5}CoSb_{0.85}Sn_{0.15}$ was studied. The microstructure of the compounds was stable even after 500 heating and cooling cycles, achieving a figure of merit of zT = 1.1.

Half-Heusler (HH) compounds with the general formula XYZ (where X and Y are transition metals, and Z is a main group element) crystallize in the cubic space group $F\bar{4}3m$ (216, *MgAgAs* structure type). Those with 18 valence electrons in the primitive cell exhibit semiconducting properties [1]. They are very promising candidates for thermoelectric (TE) energy conversion in the mid-temperature range. The advantages are their environmentally friendly constituents, thermal stability, low cost, and guaranteed future availability of raw materials.

The efficiency of TE devices is determined by their thermoelectric figure of merit zT, which depends on the operating temperature T and on the transport properties of the materials: the Seebeck coefficient S, the electrical conductivity σ, and the thermal conductivity κ, which consists of a lattice κ_l and electronic κ_e component:

$$zT = \frac{S^2\,\sigma}{\kappa_l + \kappa_e}\,T$$

Several approaches are used to optimize zT, such as tuning the carrier concentration n by partially heterovalent substitution of the main group element Z [2] and reducing the κ_l by nanostructuring or isoelectronic substitution, which introduce a mass fluctuation disorder that leads to a reduction of κ_l or phase separation [3,4].

Improved TE properties of *p*-type Half-Heusler via phase separation

Figs. 1a-d show the temperature dependence of the thermoelectric properties of the series $Ti_{1-x}Hf_xCoSb_{0.85}Sn_{0.15}$. All compounds exhibit a positive S, with a maximal value of +278 µV/°C at 700°C for $TiCoSb_{0.85}Sn_{0.15}$. All samples exhibit metallic behavior of σ, which increase from x =1 (Ti) to x = 0 (Hf). The thermal conductivity κ values are highest (4.10 WK-1m-1) for single-phase samples with x = 0 and x = 1 and effectively (> 40%) suppressed by substitution, reaching a minimal value of 2.30 $WK^{-1}m^{-1}$ at 980°C for x = 0.25. The presence of the intrinsic microstructure phase separation leads to additional boundary scattering at the interfaces and hence to a reduction of κ_l. Fine-tuning of the Ti–Hf ratio has a significant impact on zT. The selection of the optimal electronic properties in combination with the lowest thermal conductivity leads to the maximum figure of merit of zT = 1.2 at 710°C for $Ti_{0.25}Hf_{0.75}CoSb_{0.85}Sn_{0.15}$, as shown in Fig. 1d.

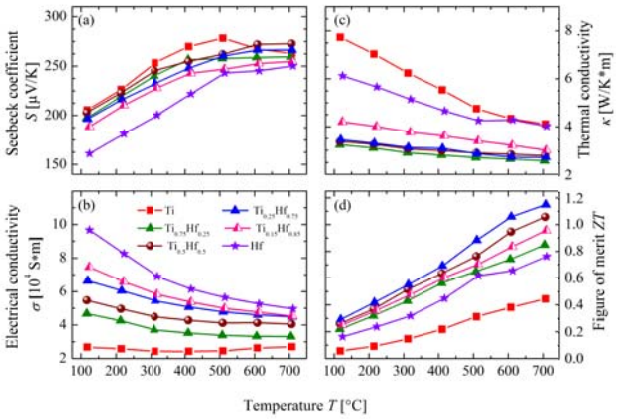

Fig. 1: Seebeck coefficient S (a), electrical conductivity σ (b), thermal conductivity κ (c), and figure of merit of $Ti_{1-x}Hf_xCoSb_{0.85}Sn_{0.15}$.

Optimization of the charge carrier concentration

The carrier concentration of the *p*-type half-Heusler alloy $Ti_{0.3}Zr_{0.35}Hf_{0.35}CoSb_{1-x}Sn_x$ was optimized by partial substitution of Sb by Sn. The interdependence of the thermoelectric properties at 610°C as a function of the carrier concentration n are shown in Fig. 2. As one expects, the electrical conductivity increased with increased charge carriers n, while the Seebeck coefficient decreased and thermal conductivity

increased slightly. It proves that the best compromise for high power factors $S^2\sigma$ is reached at x = 0.15, which yields the maximum figure of merit zT = 0.79. This is an enhancement of 40% compared to 0.57 for x = 0.1 or x = 0.2.

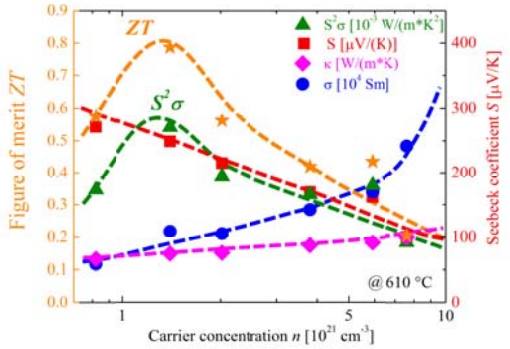

Fig. 2: *Thermoelectric properties of the p-type half-Heusler compound $Ti_{0.3}Zr_{0.35}Hf_{0.35}CoSb_{1-x}Sn_x$ as a function of the carrier concentration n at 610°C [3].*

Long-term stability

For TE applications, the thermal stability is an important aspect that should not be neglected. Here we study the reliability of the thermoelectric performance of half-Heusler $Ti_{0.5}Hf_{0.5}CoSb_{0.85}Sn_{0.15}$ under thermal cycling with up to 500 heating and cooling cycles in the temperature range from 100°C to 700°C. The effect of thermal cycling upon the thermoelectric performance of half-Heusler materials was investigated and correlated with the impact on the structural properties.

Microstructural investigations of the composition $Ti_{0.5}Hf_{0.5}CoSb_{0.85}Sn_{0.15}$ by SEM and EDX (as shown in Fig. 3a) prove that the as-cast sample underwent an intrinsic phase separation into two half-Heusler phases: Ti-rich and Hf-rich compositions. The characteristic microstructure was already obtained in the as-cast samples and was not affected by the consequent annealing steps (Fig. 3b). The microstructure was stable even after 500 heating and cooling cycles (Fig. 3c). The as-cast sample exhibited a higher thermal conductivity that decreased slightly after annealing, but the values stabilized and lay within the measurement error after annealing and further heat treatment leading to lower values. The intrinsic phase separation, which is responsible for the outstanding thermoelectric properties, was stable upon repeated heating and cooling. The value of zT was also stable upon thermal cycling (Fig. 3d) and reached the same values of 1.2 with progressing heat treatment.

References

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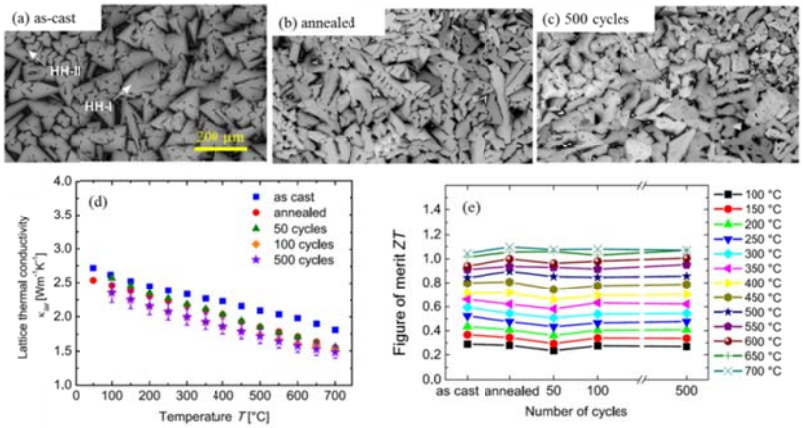

Fig. 3: Backscattered electron images (BSE) of the half-Heusler $Ti_{0.5}Hf_{0.5}CoSb_{0.85}Sn_{0.15}$ (a,b,c), lattice thermal conductivity asa function of temperature (d), and zT asa function of the number of cycles (e).